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EFFECT OF RADIATION ON GLASSES IN BOROSILICATE AND BORON-LEAD-SILICATE SYSTEMS

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The effect of an electron flux and gamma radiation on glasses produced in a synthetic glass batch is considered. The origin of the radiation color centers arising in glasses and the disintegration of these centers in thermal and photodecolorization is investigated.

Numerous fundamental problems of radiation physics of glass are not yet solved and mostly exist in the experimental phase. Data on the radiation-physical and radiation-chemical aspects of action of high-energy radiation on glass are being rapidly accumulated at present [1].

It is known that silicate, borate, and phosphate glasses used as protection from gamma radiation have a certain level of radiation-optical stability (patents: East Germany No. 2559263, U.S. No. 5057464, Japan Nos. 45–27426 and 55–42946, Bulgaria No. 25961) along with a high linear attenuation factor [1 – 4]. A diametrically opposite property of glasses used as absorption dosimeters is an increase in their optical density (darkening of glass) after being irradiated, which is a consequence of the formation of different types of color centers [1, 5].

The present paper considers the results of experimental studies of the effect of an electron flux and gamma radiation on glasses in the $Na_2O - B_2O_3 - SiO_2$ and $Na_2O - B_2O_3 - PbO - SiO_2$ systems obtained on the basis of synthesized batches.

The batches used for the production of experimental glasses were synthesized in accordance with the method developed by the authors (USSR Inventor's Certif. No. 1640923). Glasses of the $Na_2O - B_2O_3 - PbO - SiO_2$ system are obtained by hydrolysis of tetraethoxysilane in the presence of alkaline sodium ethylsiliconate with subsequent formation of lead hydroxide in this medium from lead nitrate solution, whereas subsequent introduction of boric acid solution or sodium borate into the composition accelerates the formation of gel. The mechanism of glass batch synthesis in the $Na_2O - B_2O_3 - SiO_2$ system consists in the polymerization of sodium tetraborate, which exists in the anion form in the solution and is obtained in reactions between the dimeric molecules of sodium ethylsiliconate and the boric acid solution; the content of silicon dioxide in the composition was adjusted by introducing tetraethoxysilane into the composition.

The experimental glasses (Table 1) were melted in a laboratory muffle resistance furnace in 100 ml corundum crucibles. The experimental samples were obtained by casting in metal molds and subsequent annealing. The annealed samples were subjected to mechanical treatment (grinding and polishing) to achieve an equal thickness.

It is known [6] that radiation of glasses leads to a reversible modification of their optical properties.

The effect of a fast electron beam and γ-radiation on the optical characteristics of the synthesized glasses was studied, and special attention was paid to the nature of the color centers (CC) forming in the glasses.

When glass is radiated with fast electrons, radiation defects are formed due to the kinetic energy of the electrons, and at the same time electrons are injected into the volume of glass. The generally accepted interpretation of the absorption spectra of CC in irradiated sodium-silicate glasses is based on electron CC bands in the range of 3.7 – 5.3 eV (233 – 335 nm) and hole CC bands in the range of 2.0 – 2.8 eV (440 – 620 nm) [7].

A hole localized on a nonbridge oxygen atom is the most typical hole CC.

The light transmission boundary in experimental glass 1 is located at 308 nm (Fig. 1). Radiation of this glass using an electron flux with energy of 1 MeV and an absorbed dose of 2 MGr results in a shift of the light transmission boundary to-

TABLE 1

Glass	Mass content, %			
	SiO_2	B_2O_3	Na_2O	PbO
1	32.8	65.1	2.1	–
2	29.7	20.1	4.0	46.2

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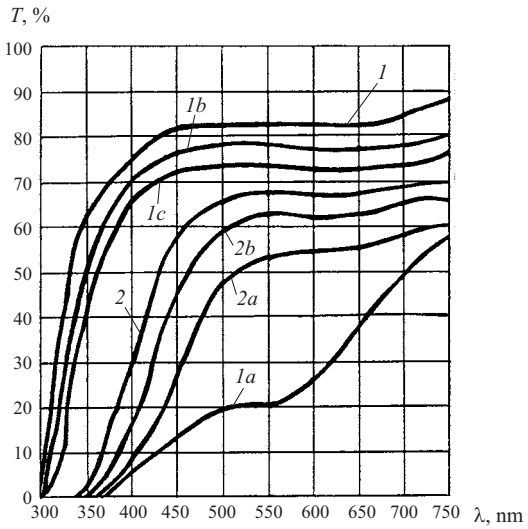

Fig. 1. Transmission spectra of glasses 1 (*1*) and 2 (*2*) radiated with an electron flux (*1a*, *2a*) and decolorized using the thermal (*1b*, *2b*) and optical (*1c*, *2c*) methods.

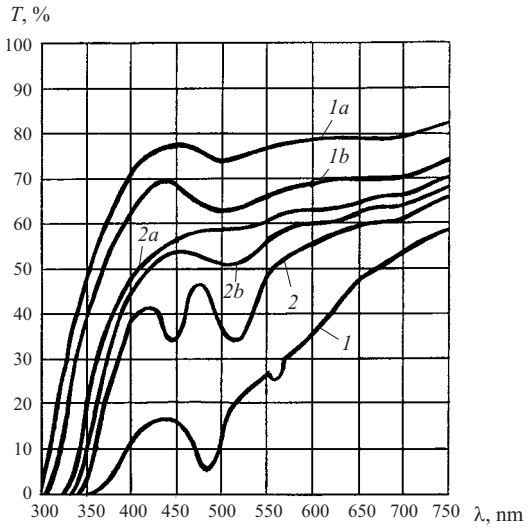

Fig. 2. Transmission spectra of γ-radiated glasses 1 (*1*) and 2 (*2*) decolorized by the thermal (*1a*, *2a*) and optical (*1b*, *2b*) methods.

ward the long-wave range up to 360 nm (Fig. 1, curve *1a*). The most intense induced CO and light absorption in radiated glass 1 are registered in the violet – blue – green – yellow range of the spectrum (430 – 550 nm). In can be assumed that the Si – O – Si bond is ruptured under the effect of electron radiation, and ≡Si – O• free radicals are formed.

The light transmission in the range 430 – 550 nm in radiated glass decreases by 50 – 55%, whereas in the red range of the visible spectrum (720 – 740 nm) it decreases by 35 – 38%.

The light transmission boundary in experimental samples of glass 2 passes at 350 nm. After the action of an electron flux and an equivalent absorbed dose it shifts somewhat (by 20 – 25 nm) to the long-wave range (Fig. 1, curve *2a*). The decrease in the light transmission does not exceed 12 – 14%

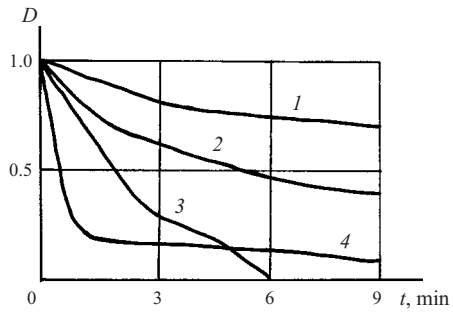

Fig. 3. Kinetics of CC disintegration in glass 1 in heat treatment [*1*, *2*, and *3*) 473, 573, and 673 K, respectively] and in photodecolorization using a DKSSh-1000 lamp (*4*).

for the whole boundary of the visible spectrum; consequently, the presence of lead in the borosilicate matrix significantly suppresses the radiation coloring of glass. This could be a result of compensation of excess negative charge in the electron traps, for instance, at the lattice points [BO_3] and [BO_4] and on the nonbridge oxygen atoms, for example, ≡Si – O•. Another possibility is a recombination of holes with Pb^{2+} cations, which are also capable of compensating excess negative charge in the tetrahedral oxide groups [8].

The obtained glass samples were subjected to γ-radiation with a ^{60}Co source up to doses of about 2 MGr. An analysis of the spectral characteristics of glass 1 revealed two main absorption bands with maxima at 495 and 562 nm (Fig. 2). The additional absorption spectrum of glass 2 induced by γ-radiation is formed by two main absorption bands at 450 and 515 nm.

When heated, glasses subjected to electron and γ-radiation become decolorized, and the shape of their transmission spectra is modified. The absorption bands of glasses 1 and 2 γ-radiated and thermally decolorized for 60 min at 473 K are characterized by stable maxima at 495 and 515 nm, respectively, whereas the absorption bands at 562 and 450 nm are unstable. A further increase in temperature leads to intense disintegration of CC in the range 470 – 540 nm, and at a temperature of 623 K, 90 – 95% of these CC disintegrate. Thus, the distinction of stable and unstable CC is only true for a specific temperature range.

The model of the process is usually deduced from the shape of the CC disintegration curve [7]. It can be seen from the obtained data (Fig. 3) that the disintegration kinetics of CC is essentially nonexponential. As the temperature increases, the equilibrium concentration of CC decreases and the rate of their disintegration increases. It is noted [7] that the kinetics of disintegration of CC should be described by the simplest equations derived from the assumption of the mono- and bimolecular nature of the process, which leads to a solution in the form of an exponential or a hyperbolic function.

The experimental results of studying the kinetics of CC disintegration in glass 1 demonstrate that various types of CC affect the deviation of the kinetic curve from an exponen-

tial or a hyperbolic curve in the course of thermal disintegration of CC.

The photodecolorization of radiated experimental glasses was performed using a light beam, in particular, a DKSSh-1000 lamp for 10 min. The spectral transmission of glasses 1 and 2 after photodecolorization (Figs. 1 and 2) is restored on the average to the level of 85 and 88% in the ranges 330 – 650 and 720 – 740 nm, respectively.

It can be assumed that photometric release of charge carriers from CC electron traps using a visible light beam is possible in a silicate matrix of the glass. The release of charge carriers from borate and lead-borate anion complexes in glass is hampered, since as a result of electron radiation of experimental glasses, the electron CC and especially the hole CC arising in glass are resistant to the optical effect.

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